

theory. The Racah parameters  $B$  and  $C$  decrease with increasing pressure. This can be attributed to spreading of the  $3d$  orbitals, including an outward movement of the radial maximum, which reduces the interelectronic repulsion. We shall refer to this phenomenon in our later discussion.

Generally, energy levels in a complex can be best described in terms of a molecular orbital diagram as shown in Fig. 1. The predominantly metallic antibonding levels  $t_{2g}$  and  $e_g$ , as well as their separation  $10 Dq$ , are marked. As shown, it is possible for the  $t_{2g}$  orbital to form a pi bond with excited ligand orbitals which tends to stabilize it (i.e., lower its energy) by a modest amount. This fact will also be of use to us later.

In addition to the absorption peaks mentioned above, there appear very intense peaks centered at about 3–4 eV (24,000–32,000  $\text{cm}^{-1}$ ), with tails which may extend through the visible region. These correspond to ligand-to-metal charge transfer. In Fig. 1 such transfer is indicated from the non-bonding

ligand  $t_{2u}$  level to the metallic  $t_{2g}$  state. These peaks shift to lower energy by as much as an electron volt in 100 kilobars. There are at least two apparent causes for this red shift. In the first place, the pi bonding tends to increase with pressure faster than the sigma bonding, lowering the energy of the  $t_{2g}$  level vis-à-vis the ligand levels. The calculations of Lewis (3) show that this is a factor, but probably not the dominant one. In the second place, the spreading of the  $3d$  electrons mentioned above lowers the energy of the  $3d$  states substantially. This, in fact, is probably the major contribution (3, 10).

#### IV. The Reduction of Ferric Ion

As mentioned in the introduction, it has been found that the reversible reduction of Fe(III) to Fe(II) with increasing pressure is an ubiquitous phenomenon. We shall discuss first a few examples, together with an analy-

sis of the process, and then present some special cases of unusual interest.

Fig. 2 shows conversion data for  $\text{FeCl}_3$ ,  $\text{FeBr}_3$ , and  $\text{KFeCl}_4$ . The first two compounds have slightly distorted octahedral symmetry, while in  $\text{KFeCl}_4$  the iron is in a tetrahedral site. The equilibrium constant

$$K = \frac{C_{\text{II}}}{C_{\text{III}}}$$

where  $C_{\text{II}}$  and  $C_{\text{III}}$  are the concentrations of Fe(II) and Fe(III) sites including the ligands. The linear relationship between  $\ln K$  and  $\ln P$  is very general. Constants  $A$  and  $B$  for the equation  $K = AP^B$  are listed in Table 1 for a large number of compounds. There is clear evidence that these results represent equilibrium and not the result of slow kinetics. In the first place, consecutive runs at the same pressure gave essentially identical results. In the second place, when pressure was increased, as soon as a spectrum became resolved on the oscilloscope (5–15 minutes) the increased conversion was evident and remained constant with time, although complete runs took 8–48 hours or longer.

One can present a straightforward thermodynamic analysis:

$$K = \exp \left( - \frac{\Delta \bar{G}}{RT} \right) \quad (1)$$

$$\frac{\partial \ln K}{\partial \ln P} = \frac{P \Delta \bar{V}}{RT} = \frac{P(\bar{V}^{\text{III}} - \bar{V}^{\text{II}})}{RT} = B \quad (2)$$

where  $\bar{V}^{\text{III}}$  and  $\bar{V}^{\text{II}}$  represent the partial molar volumes of the Fe(III) and Fe(II) ions with their associated ligands. A slight rearrangement of Eq. 2 gives:

$$\frac{\partial \ln C_{\text{II}}}{\partial \ln P} = \frac{P(\bar{V}^{\text{III}} - \bar{V}^{\text{II}})}{RT} C_{\text{III}} \quad (3)$$

The fractional increase in concentration of reduced sites per fractional increase in pressure is proportional to the concentration of sites available for conversion. The coefficient of proportionality is the work to convert a site measured in thermal units (units of  $RT$ ). It is perhaps surprising that this is independent of pressure, i.e., that the volume change accompanying reduction is inversely proportional to the pressure, and this may be true only within our limits of accuracy. The pressure range over which its validity has been established is 10–200 kilobars. Also, conversions less than 6–7% or

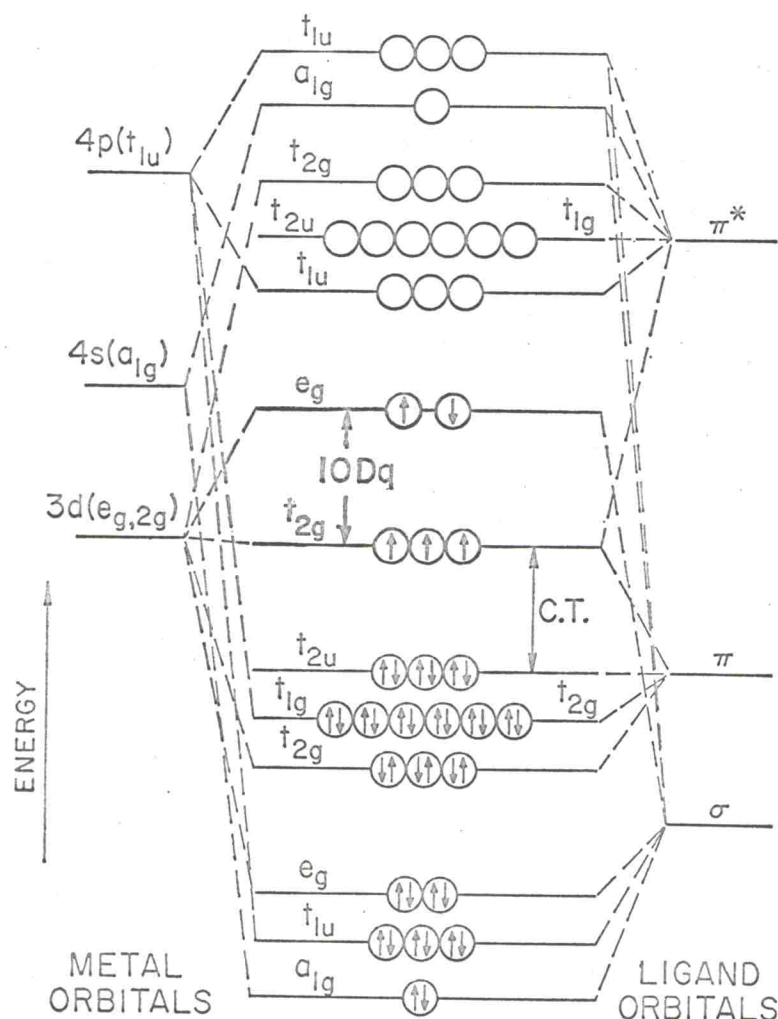


Fig. 1. Molecular orbital diagram—Octahedral symmetry